ANALYSIS OF FLUIDIZED BED COMBUSTION SAMPLES TO STUDY THE DEGREE OF HYDRATION OBTAINED USING THE CERCHAR HYDRATION PROCESS

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ABSTRACT

Analyses were performed on samples of fly ash and bottom ash from a fluidized bed combustor from CANMET, before and after being treated with a hydration process by CERCHAR (France). The results indicate that the process effects a conversion of CaO to $Ca(OH)_2$ of 90% or more. The available methods for the analysis of lime in the presence of silicates do not allow a better precision.

TABLES

Table 1a - Major components, except S and C, expressed as oxides per cent of sample.

Table 1b - Minor components.

Table 2 - Analysis of carbonate.

Table 3 - Analysis of total sulphur and soluble sulphate.

Table 4 - Alkalinity titration and calcium balance.

Table 5 - Calcium compounds.

Table 6 - X-ray diffraction.

Table 7 - Composition of the samples in terms of chemical compounds.

Table 8 - Analytical methods.

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Table 10 - Percentage of conversion of CaO into $Ca(OH)_2$.

I - METHODS AND SAMPLES

METHODS

COMPONENT	UNITS	METHOD	DETECTION LIMIT
Major components	%	XRF	0.01
Trace components	ppm	XRF	10
CO_2	%	COMB-COULOM	0.01
Ca	%	XRF, NA & ICP	0.01
$Ca(OH)_2$	%	TGA	1
CaO(free)	%	WC	0.01
Ca silicates	%	WC	0.1
S	%	WC	0.01
SO_4	%	WC	0.1
Crystalline compounds	semi-quantitative	XRD	3 to 5%

COMB: combustion; COULOM: coulometry; ICP: induced current plasma; NA: neutron activation; TGA: thermogravimetry; WC: wet chemistry; XRD: X-ray diffraction; XRF: X-ray fluorescence.

All significant results reported were obtained by duplicate analyses and in some cases several methods were applied.

SAMPLES

FA (# 8992) - Baghouse or fly ash.

FA-T (# 8710) - Baghouse or fly ash, treated by the CERCHAR (France) hydration process.

BA (# 8993) - Bed or bottom ash.

BA-T (# 8704) - Bed or bottom ash, treated by the CERCHAR (France) hydration process.

All samples were ground to 200 mesh and dried at 105°C for 2 hours; all results are expressed on dry basis.

Samples FA and BA are from CANMET's Mineral Sciences Laboratories (MSL) pilot scale circulating fluidized bed combustor.

II - ANALYSES

MAJOR COMPONENTS

Table 1 - Major components, except S and C, expressed as oxides per cent of sample.

Sample:	FA	FA-T	BA	BA-T
SiO_2	11.9	11.0	34.0	33.8
CaO	42.6	40.5	39.4	37.0
Al_2O_3	5.32	4.82	4.50	5.12
MgO	0.80	0.74	0.71	0.70
Na_2O	0.1	0.08	0.05	0.09
K_2O	0.52	0.44	0.48	0.62
Fe_2O_3	10.5	9.80	4.72	5.24
MnO	0.09	0.08	0.07	0.07
TiO_2	0.21	0.19	0.18	0.21
P_2O_5	0.05	0.05	0.05	0.04
LOI	13.3	18.9	3.85	6.77
Sum	85.4	86.7	88.1	89.7

Comments - The percentages recorded correspond to the total content in the samples, in whatever chemical combination. LOI: loss on ignition, performed at 950°C.

MINOR COMPONENTS

Table 1b - Minor components, in ppm.

Sample:	FA	FA-T	BA	BA-T
Cr	<10	<10	16	132
RB	35	11	28	30
Sr	225	214	215	219
Y	16	<10	<10	32
Zr	44	53	28	40
Nb	18	32	11	<10
Ba	277	257	153	132

CARBONATE

Table 2 - Analysis of carbonate.
(% referred to dry sample)

Sample:	FA	FA-T	BA	BA-T
Carbonate as CO_2	2.60	2.75	0.49	0.62
Carbonate as $CaCO_3$	5.92	6.26	1.11	1.41

Comments - Assuming that essentially all the carbonate is $CaCO_3$, the last line of data is obtained.

The data for the treated samples are slightly higher than for the untreated ones, although the treatment implies some dilution. This suggests a certain amount of absorption of CO_2 by the treated samples.

SULPHUR COMPOUNDS

Table 3 - Analysis of total sulphur and soluble sulphate.
(% referred to dry sample)

Sample:	FA	FA-T	BA	BA-T
Total sulphur as S	5.88	--	4.83	--
Total sulphur as $SO_4^=$	17.6	--	14.4	--
Soluble sulphate as $SO_4^=$	16.2	15.1	14.8	13.5
Soluble sulphate as $CaSO_4$	22.97	21.4	20.98	19.10

Comments - The second and third lines of data for FA and BA are close, indicating that most or all of the sulphur is present as "soluble sulphate" (defined according to the procedure of Norm ASTM C25-81a, Paragraph 100). Considering that the sulphate must be in the form of $CaSO_4$, the data of the last line have been calculated.

ALKALINITY TITRATION AND CALCIUM BALANCE

Table 4 - Alkalinity titration and calcium balance.
All figures expressed as CaO%.

Sample:	FA	FA-T	BA	BA-T
Titration	33.4	30.3	29.4	26.4
$CaSO_4$	9.5	8.8	8.7	7.9
Sum	42.9	39.2	38.0	34.3
Total Ca	43.1	40.8	38.2	35.9
(Sum/Total Ca)%	99.5	96.1	99.5	95.5

Comments - The acidimetric determination of alkalinity was performed by using an excess of acid and back titrating the excess. This includes $CaCO_3$, CaO, $Ca(OH)_2$ and Ca silicates.

The $CaSO_4$ has been obtained from Table 3 and expressed as CaO.

The total calcium has been taken as the average of the X-ray fluorescence determination quoted in Table 1 and two or three other independent determinations, by X-ray fluorescence, Neutron activation and Induced current plasma.

Considering that $CaSO_4$ is the only calcium compound present which is not included in the titration, the sum of the titration and $CaSO_4$ should be equal to the total calcium, independently determined, if all figures are expressed as CaO. The check gives consistency within 5%.

CALCIUM COMPOUNDS

The analytical methods utilized to derive the distribution of calcium in various compounds are considered in the Discussion. Here only the results are collected in Table 5.

Table 5 - Calcium compounds.
All figures expressed as CaO%.

Component \ Sample	FA	FA-T	BA	BA-T
CaO	20.7 (21.5)	-0.2 (1.4)	18.8 (18.2)	1.1 (1.9)
$Ca(OH)_2$	-	18.3	-	14.7
$CaCO_3$	3.3	3.5	0.6	0.8
$CaO.SiO_2$	7.0	6.2	6.0	4.6
Soluble silicates	2.5 (1.7)	2.6 (1.0)	4.0 (4.5)	5.2 (5.2)
$CaSO_4$	9.5	8.8	8.7	7.9

Note: figures between brackets correspond to results obtained using the sucrose method.

X-RAY DIFFRACTION

Table 6 - X-Ray diffraction.

FLY ASH	MAJOR:	LIME, ANHYDRITE
	MINOR:	HEMATITE
	TRACE:	QUARTZ, CALCITE
FLY ASH	MAJOR:	ANHYDRITE, PORTLANDITE
TREATED	TRACE:	QUARTZ, CALCITE, HEMATITE
BOTTOM ASH	MAJOR:	QUARTZ, LIME
	MINOR:	ANHYDRITE
	POSSIBLE TRACE:	HEMATITE
BOTTOM ASH	MAJOR:	QUARTZ
TREATED	MINOR:	PORTLANDITE, ANHYDRITE
	POSSIBLE TRACE:	HEMATITE

Comments - Lime (CaO), appearing as a major component in the untreated samples of fly ash and bottom ash, has completely disappeared in the treated samples. No calcium silicate has been detected in any of the four samples.

CHEMICAL COMPOUNDS

Table 7 - Composition of the samples in terms of chemical compounds. (% referred to dry sample)

Sample:	FA	FA-T	BA	BA-T
$CaSO_4$	23.0	21.4	21.0	19.1
$CaCO_3$	5.9	6.3	1.1	1.4
CaO	20.7	0.0*	18.8	1.1
$Ca(OH)_2$	-	24.2	-	19.4
$CaO.SiO_2$	14.5	12.8	12.4	9.5
Soluble Ca silicates	3.8	4.0	6.1	8.0
$Others_{corr}$	19.3	17.8	34.1	35.4
LOI_{corr}	10.7	11.7	3.4	2.6
Sum	97.9	98.2	96.9	96.5

*The small negative value of Table 5 is taken here as a 0 value.

Comments - The soluble Ca silicates have been calculated as dicalcium silicate ($2CaO.SiO_2$), in order to give an estimative percentage, but the relative proportions of the various soluble silicates in this group are unknown.

LOI_{corr} is the loss on ignition corrected from the losses of water and carbon dioxide, already included in $Ca(OH)_2$ and $CaCO_3$:

$$LOI_{corr} = LOI - (H_2O/Ca(OH)_2) \times Ca(OH)_2\ \% - CO_2\ \%$$

$$= LOI - 0.243\ Ca(OH)_2\ \% - CO_2\ \%$$

$Others_{corr}$ is the sum of all the components (SiO_2, Al_2O_3, Fe_2O_3, etc.) not included in the previous compounds, corrected for the SiO_2 already included in $CaO.SiO_2$ and soluble Ca silicates:

$$Others_{corr} = Others - (SiO_2/CaO.SiO_2) \times CaO.SiO_2\ \% - (SiO_2/2CaO.SiO_2) \times \text{Soluble Ca Silicates}\ \%$$

$$= Others - 0.517\ CaO.SiO_2\ \% - 0.349\ \text{Soluble Ca silicates}\ \%$$

III - DISCUSSION

1 - RESULTS FROM X-RAY DIFFRACTION

X-ray diffraction is indeed a powerful analytical tool to help in the interpretation of results, but it has some serious limitations. It reveals the well formed crystalline compounds, but not the amorphous components, whose presence is revealed by diffuse "humps" in the diffractograms rather than by defined peaks. Moreover, crystalline material in a highly subdivided microcrystalline structure may not be revealed at all.

Thus, silicates are not seen in the diffractograms, although some silicates, like kaolinite, must be frequently present and relatively abundant (raw materials containing clay). Secondly, in none of the 4 samples which are the object of this study, was it possible to detect any of the calcium silicates, although the chemical study indicates their presence and in spite of the fact that wollastonite (monocalcium silicate: $CaO.SiO_2$ or $CaSiO_3$) is clearly observable in other materials.

2 - ANALYSIS OF CALCIUM COMPOUNDS

Since the hydraulic properties of the material depend essentially on the calcium compounds, particularly the free CaO, it is of paramount importance to estimate the distribution of calcium into the different compounds present: CaO, $Ca(OH)_2$ (in slaked samples), $CaCO_3$, $CaSO_4$, CaS (if any), and the various calcium silicates.

Some of these compounds are derived readily from different analyses and simplifying assumptions:

- $CaCO_3$ from the determination of CO_2.
- CaS from the determination of $S^=$ (assuming that no other sulphides are present).
- $Ca(OH)_2$ from thermogravimetric analysis.

- $CaSO_4$ from the determination of soluble $SO_4^=$ (assuming that no other soluble sulphates are present).

The 4 samples now analyzed have very small concentrations of sulphide; therefore we shall simplify the discussion by ignoring CaS.

The knowledge of the sample after the determinations mentioned above is yet incomplete. Besides these determinations, we apply in all cases a titration that will include all the compounds capable of acting as a base in acid treatment. The procedure consists in treating the sample with 1 N HCl, filtering and back titrating the liquid with 1 N NaOH and phenolphthalein. This is an exact and reliable determination, and it includes all calcium compounds except the sulphate:

- CaO ($CaO + 2\ H^+ = Ca^{++} + H_2O$)
- $Ca(OH)_2$ ($Ca(OH)_2 + 2\ H^+ = Ca^{++} + 2\ H_2O$)
- $CaCO_3$ ($CaCO_3 + 2\ H^+ = Ca^{++} + CO_2 + H_2O$)
- CaS ($CaS + 2\ H^+ = Ca^{++} + H_2S$)
- $CaO.SiO_2$ ($CaO.SiO_2 + 2\ H^+ = Ca^{++} + H_2O + SiO_2$)
- $2CaO.SiO_2$ ($2CaO.SiO_2 + 4\ H^+ = 2\ Ca^{++} + 2\ H_2O + SiO_2$)
- $3CaO.SiO_2$ ($3CaO.SiO_2 + 6\ H^+ = 3\ Ca^{++} + 3\ H_2O + SiO_2$)
- $3CaO.2SiO_2$ ($3CaO.2SiO_2 + 6\ H^+ = 3\ Ca^{++} + 3\ H_2O + 2\ SiO_2$)

Whatever Al_2O_3 and Fe_2O_3 that becomes dissolved during the acid attack is re-precipitated before reaching the phenolphthalein turning point, and therefore cancels out in the titration result. Thus, this titration plus the $CaSO_4$, everything expressed in terms of CaO, should be equal to the total calcium (also as CaO), as determined by an independent method (for instance, X-ray fluorescence or neutron activation). This check was performed as indicated in Table 4.

The central problem in this study is to derive the contents of CaO and $Ca(OH)_2$. For that, we consider now the analytical methods that can be used for all the

compounds that are included in the titration procedure already mentioned. They are summarized in Table 8.

Table 8 - Analytical methods.

Method \ Compound	CaO	$Ca(OH)_2$	$CaCO_3$	$CaO.SiO_2$	Soluble Ca Silicates
[1]Dissolution in acid and back titration.	X	X	X	X	X
[2]Titration at pH ≥ 8	X	X	1/2		X
[3]Glycerine or sucrose	X	X			
[4]TGA		X			
[5]CO_2 determination			X		

≈CaO = 3-4

$CaO.SiO_2$ = 1-2-(1/2)5

Soluble silicates = 2-3-(1/2)5

As can be seen, the 3 first procedures measure the content of several components at the same time. However, 5 determinations are made and there are 5 component percentages to be derived; the problem is therefore well defined, at least within the degree of reliability of the data. It will be observed that:

- $CaO.SiO_2$ is obtained from the difference 1 - 2 - (1/2) 5 (where the digits indicate the procedure)
- CaO is obtained from 3 - 4

- Soluble silicates are obtained from 2 - 3 - (1/2) 5

Unfortunately, the distinction between these remaining compounds is a difficult analytical problem, and some of the available methods are at best only approximate.

For instance, the ASTM method of the sucrose to determine $CaO + Ca(OH)_2$ depends on the difference in neutralization velocity of the lime with the reaction velocity of calcium silicates; this is in turn dependent on such parameters as the state of subdivision of the sample. Both this method, and the glycerine-methanol method as described by Fresenius and Jander (Handbuch der analytischen Chemie) have been used. However, it was found that, at least for the matrices of the 4 samples studied, the latter method requires a correction factor. Thus the results obtainable for $[CaO + Ca(OH)_2]$ carry a certain amount of uncertainty. Within these limitations, an estimation of the content in free CaO can be obtained by subtracting the $Ca(OH)_2$ obtained by TGA (thermogravimetric analysis) from the results of either the glycerine-methanol or the sucrose method. In Tables 5 and 9 the results from the sucrose method are given between brackets.

The remaining concentration of calcium compounds to make up for the total value obtained by acid dissolution and back titration must be attributed to other compounds than those already considered (CaO, $Ca(OH)_2$ and $CaCO_3$). Given the nature of the samples, this difference is attributed to calcium silicates, possibly preexistent in the raw material and perhaps monocalcium silicate that may have been produced during the combustion. Unfortunately, these compounds could not be detected by X-ray diffraction in these 4 samples, as mentioned before.

Assuming however that this assignment is essentially correct, it must be kept in mind that there may be several silicates:

$CaO.SiO_2$ or monocalcium silicate (wollastonite). Soluble in acids but not in water.

$2CaO.SiO_2$, soluble in water, more or less slowly.

$3CaO.SiO_2$, soluble in water, more or less slowly.

$3CaO.2SiO_2$, soluble in water, more or less slowly.

In this study only the water insoluble monocalcium silicate has been differentiated from the others, considered as "soluble silicates". This distinction may be important in reference to the hydration process, since the monosilicate is not attacked by water, while the soluble silicates react as follows:

$$2\,(2CaO.SiO_2) + 4\,H_2O = 3CaO.2SiO_2.3H_2O + Ca(OH)_2$$

$$2\,(3CaO.SiO_2) + 6\,H_2O = 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2$$

Because of the insolubility of $CaO.SiO_2$ in neutral or alkaline solutions, it is possible to titrate everything except this silicate, by introducing the sample in water at about 80°C and titrating slowly with strong stirring while keeping a slightly alkaline reaction to phenolphthalein. The procedure takes several hours, because of the slow solubilization of the soluble silicates. This procedure has been called the "Titration at pH > 8". It may be remarked that only half of the carbonate is neutralized, because at this pH it is transformed into HCO_3^-, rather than $CO_2 + H_2O$. The results of the 5 determinations have been collected in Table 9, while the concentrations derived for all the calcium compounds were given in Table 5.

Table 9 - Results.
All figures expressed as CaO%.

Method \ Sample	FLY ASH	FLY ASH TREATED	BOTTOM ASH	BOTTOM ASH TREATED
[1]Dissolution in acid and back titration.	33.4	30.3	29.4	26.4
[2]Titration at pH ≥ 8	24.8	22.4	23.1	21.4
[3]Glycerine-methanol (sucrose)	20.7 (21.5)	18.1 (19.7)	18.8 (18.2)	15.8 (16.6)
[4]TGA	-	18.3	-	14.7
[5]CO_2	3.3	3.5	0.6	0.8

The figures between brackets indicate the results obtained when the sucrose method is applied to CaO + $Ca(OH)_2$; otherwise the results from the glycerine-methanol method are used.

Several remarks are to be made regarding these two tables. The methods of glycerine-methanol (with correction factor) and of sucrose give fairly consistent results, and these amount to around 10% less than the results of the back titration method, the difference to be accounted for by silicates.

Both for fly ash and for bottom ash, the sum of [CaO + $Ca(OH)_2$] after treatment should be expected to be equal to the initial CaO divided by 1.20 (to account for the dilution effected by the addition of water). This is confirmed with good approximation (20.7/1.20 = 17.2 and 18.3 for fly ash, and 18.8/1.20 = 15.7 and (1.1 + 14.7) = 15.8 for bottom ash). The same dilution effect is observed for $CaO.SiO_2$ and for

$CaSO_4$. An opposite change is observed for $CaCO_3$ and for soluble silicates; this must be attributed to the compounded experimental errors altering somewhat these smaller percentages.

The small negative value for CaO in treated fly ash is probably due to experimental error. However, we must consider that there is the possibility of having, after hydration, more $Ca(OH)_2$ than the initially available CaO, because of the reactions of soluble silicates with water; this was not taken into consideration in our calculations and could in principle result in a negative value calculated for CaO.

It is interesting to note that, according to this study, these samples contain appreciable amounts of both monocalcium silicate and of soluble silicates, although it was not possible to identify any of these compounds by X-ray diffraction.

3 - COMPOSITION OF THE SAMPLES IN TERMS OF CHEMICAL COMPOUNDS

Table 7 gives the summary of the compounds of interest. No attempt has been made to investigate the content of quartz and silicates or silicoaluminates. The addition of the detailed contributions gives satisfactory values within a few units percent.

4 - CONVERSION OF LIME

The important conclusion of the set of analyses is that the conversion of CaO to $Ca(OH)_2$ by the applied hydration procedure seems to be above 90%. These results are given in Table 10.

Table 10 - Percentage of conversion of CaO into $Ca(OH)_2$.

Figures between brackets correspond to method of sucrose.

FLY ASH:	100%	(93%)
BOTTOM ASH:	93%	(89%)

5 - CONCLUSIONS AND RECOMMENDATIONS

The hydration process tested appears to have been successful in producing at least 90% of lime conversion and probably more.

It must be stressed that the required analytical methods have a certain degree of uncertainty and it would be highly desirable to adjust their performance by tests with standards and spiked samples, so as to obtain reliable procedures for the identification and quantification of calcium silicates and calcium oxide. Time limitations did not allow this work to be done, which was beyond the scope of the present study.